Study of Molecular Arrangement and Surface Morphology of Organized Molecular Films of Charge-Transfer Complexes Containing Metal(dmit)$_2$ Unit

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The molecular arrangement and surface morphology of organized molecular films of alkylammonium-M bis(1, 3-dithiole-2-thione-4, 5-dithiolate) ((dmit)$_2$, $M = \text{Ni}$, Au, and Pd) charge-transfer complexes were investigated by using the surface pressure–area isotherm, in-plane and out-of plane X-ray diffractions (XRD), and atomic force microscopy. In the bulk state, several alkylammonium-M(dmit)$_2$ molecules could not form a highly ordered layer structure along the $c$-axis and a sub-cell structure of the alkyl chain in the $ab$-plane; however, almost all molecules formed a layer structure in the film multilayers. Monolayers of alkylammonium-M(dmit)$_2$ salts on the water surface were relatively condensed. Out-of plane and in-plane XRD measurements revealed that over a long period, systematic changes occurred in the changes appear to be caused by enhancement of the van der Waals interaction among long hydrocarbons and the $\pi-\pi$ interaction among M(dmit)$_2$ units arranged two-dimensionally. In addition, both the molecular arrangement and the morphology of the films showed dependence on the hydrocarbon length, number of alkyl chains, and kind of central metal. In particular, the molecular arrangement of materials having didecyl chains changed drastically and M(dmit)$_2$ units were highly oriented in the $ab$-plane.

Key words: alkylammonium-metal(dmit)$_2$; layer structure; two-dimensional lattice; molecular arrangement; surface morphology

1. INTRODUCTION

Alkylammonium-metal bis(1, 3-dithiole-2-thione-4, 5-dithiolate) (M(dmit)$_2$) complexes exhibit a variety of electrical properties ranging from dielectric to superconducting.$^1$ Langmuir-Blodgett (LB) films of dialkylammonium-Au(dmit)$_2$ salts exhibited a high lateral conductivity of 40–100 S/cm at room temperature after electrochemical oxidation or I$_2$ doping; these films also showed metallic temperature dependence of the conductivity.$^2$ Furthermore, the ac magnetic susceptibility and temperature dependence of the conductivity.$^2$ It has been elucidated that field-effect doping (FE doping) is an effective carrier doping method for organic semiconductors. An important requirement for achieving optimum transport characteristics is to construct a well-ordered conducting path for charge carriers, along which oriented \( \pi \)-conjugated molecular systems interact with each other in the face-to-face direction to form a stacking structure.$^6$ The LB technique is useful in controlling the molecular arrangements and in constructing the conducting path for charge carriers.$^7,8$

In a previous study, we attempted to improve conductivities of an LB film containing alkylammonium-M(dmit)$_2$ complexes by using the FE doping method.$^9$ If the mechanism of conduction of this LB film is elucidated, we can use the obtained information to fabricate novel devices. For driving the functionality of these organic molecular devices in an efficient manner, it is a prerequisite to control the molecular orientation and arrangement at the monomolecular level. However, very few studies have carried out a detailed structural estimation and morphological observation of organized molecular films of alkylammonium-M(dmit)$_2$ on the sub-nanometer scale, whereas several studies have extensively investigated conductive properties of LB films$^{10}$ and carried out a structural estimation of three-dimensional single crystals.$^5,10$

By the way, functional molecular assemblies, which are precisely controlled molecular arrangements, and their organized molecular films$^{11}$ can be developed as potential candidates for biomimetic models$^{12}$ and molecular electronic devices$^7$, which have attracted considerable interest in basic science; further, these molecular assemblies have several potential applications.

It is commonly known that long-chain compounds, which have crystallizable long hydrophobic chains attached to functional groups, are packed into a layer structure$^{13}$ along the $c$-axis and sub-cell of the long chains in the $ab$-plane.$^{14}$ This “sub-cell” structure$^3$ of the n-alkyl chain in amphiphiles is formed as a two-dimensional lattice, and the “layer structure” along the $c$-axis often reflects the large spacing between hydrophobic chains in accumulated double-layer structures.

In this study, we investigate the molecular orientation and surface morphology of organized molecular films of alkylammonium-M(dmit)$_2$ (M = Ni, Au, and Pd) salts on a solid by the surface
2. EXPERIMENTAL

2.1 Materials

Alkylammonium-M(dmit)2 salts (abbrev. (CnH2n+1)mN(CH3)4–mM(dmit)2, M = Ni, Au, and Pd), Fig. 1) were synthesized using the same procedure as that described in previous studies.9 In this study, monolayers of (C8H17)mN(CH3)4–mM(dmit)2 were spread from 10–4 M onto distilled water (18 Å/molecule) or acetonitrile/benzene (50/50, v/v) mixed solutions (approximately 10–4 M) using a RADAR diffractometer (Rigaku Co.). We show that it is possible to accurately control the molecular arrangement, packing, and regularity of the layered organization by methods of formation of organized molecular films.10

3. RESULTS AND DISCUSSION

From the results of π–A isotherms, monolayers of didodecyl(dimethylammonium-Ni(dmit)2) (abbrev. 2(C12)-Ni), diatocadecyl(dimethylammonium-Au(dmit)2) (2(C18)-Au), and didecyl(dimethylammonium-Ni(dmit)2) (2(C10)-Ni) salts formed liquid expanded surface monolayers. As compared to these four monolayers, monolayers of didodecyl-......

Fig. 2 Out-of-plane XRD profiles of multilayers of Na(C12H25)nN(CH3)4–mM(dmit)2 salts transferred by horizontal lifting method; (a) dependency on chain length and (b) plots of number of C atoms in alkyl-chain vs. long spacing and estimated molecular length of dialkyl ammonium by calculation, (c) dependency on number of chains, and (d) dependency on central metals.
multilayers of 2(C10)-Au show three layer spacings, and 2(C18)-Ni, which forms an expanded monolayer on water surface, is unable to form the layer structure along the c-axis.

In order to evaluate the ability of alkylammonium-M(dmit)₂ salts in bulk to form a layer structure, WAXD measurements were carried out. As a result, formation of a highly ordered layer structure along the c-axis is not essentially a stable feature of these charge-transfer complexes in bulk. Almost all complexes formed a peculiar two-dimensional arrangement and showed layered organization by method of organized molecular films.

Figure 3 shows in-plane XRD profiles of X-type multilayers of several alkylammonium-M(dmit)₂ salts. Multilayers of 2(C22)-Ni and 2(C18)-Ni show relatively weak signals at 4.1 Å, whereas multilayers of 2(C14)-Ni and 2(C12)-Ni show a halo and low-intensity peak at 6.8 Å. The in-plane XRD profiles of the salts show that the molecular arrangement of 2(C10)-Ni changes drastically with a change in the chain length. Figure 4 shows in-plane XRD profiles of the salts showing that the molecular arrangement of 2(C10)-Ni changes drastically with a change in the chain length. Five different in-plane spacings—8.7, 6.8, 5.2, 4.4, and 4.1 Å—are clearly confirmed in multilayer of this salt.

The in-plane spacings of 5.2 and 4.1 Å corresponded to the in-plane spacing formed by the alkyl chain judging from the results of 3(C10)-Ni and 4(C10)-Ni salts. Within the residual three peaks at 8.7, 6.8, and 4.4 Å, spacing of 8.7 and 4.4 Å probably correspond to the first and second order reflections. This highly ordered structure with a spacing of 8.7 Å was considered to be the repeating unit of the two-dimensional M(dmit)₂ arrangement. By a simple calculation, the length of the M(dmit)₂ unit along the long axis was determined to be approximately 17 Å; therefore, a two-dimensional tilted arrangement was assumed to be formed in the film of 2(C10)-Ni. In this case, tilt angle from the molecular plane was 51°. On the other hand, the

Fig. 3 In-plane XRD profiles of multilayers of (CₙH₂ₙ₊₁)mN(CH₃)₄-M(dmit)₂ salts transferred by horizontal lifting method; (a) dependency on chain length, (b) dependency on number of chains, and (c) dependency on central metals.

Fig. 4 Models of two-dimensional arrangements of (dmit)₂ units in organized molecular films and schematic illustration of layer alignment along the c-axis of (a) (C₈H₁₇)₂N(CH₃)₂-Ni(dmit)₂ and (b) (C₁₀H₂₁)₂N(CH₃)₂-Au(dmit)₂ salts.
spacings of 6.8 Å was the distance between M(dmit)₂ units facing each other. This spacing was also confirmed in the in-plane XRD profiles of 2(C14)-Ni and 2(C12)-Ni. Although the M(dmit)₂ unit is almost flat-type group, gap from the molecular plane is caused by changes in the stable configuration with a change in the radius of the covalent bond of the central metals. This model of molecular arrangement is probably accurate because the absence of highly ordered molecular pairs cannot yield two-dimensional repeating units.

Figure 4(b) shows a model of characteristic molecular orientation of (C10)-Au multilayers. In this case, we concluded that the in-plane spacings of 4.8, 4.5, and 3.9 Å correspond to that in the triclinic sub-cell of hydrocarbons. The spacings of 14.0 and 7.9 Å shown in this figure are the distances between M(dmit)₂ units in the film plane. As mentioned previously, it is supposed that gap from the molecular plane is caused by changes in the stable configuration with a change in the radius of the covalent bond of the central Au. In this case, the distance of 7.9 Å corresponds to the spacing between M(dmit)₂ units facing each other in the complex containing Au. Since the radius of the Au is larger than that of the Ni atom, it is supposed that the distortion of the molecular plane is relatively large and that the distance between (dmit)₂ pairs is large. The residual spacing of 14 Å is the two-dimensional repeating unit of coupled M(dmit)₂ units facing each other. The spacing of 14 Å is relatively large, and from the results of polarized visible spectra, it is unlikely that the M(dmit)₂ unit is arranged at a highly tilted angle with respect to the surface normal. Therefore, it is inferred that a tilt angle of 36° to the solid surface, which corresponds to an in-plane spacing of 14.0 Å, is suitable.

Figure 5 shows AFM images of X-type monolayers for several alkylammonium-M(dmit)₂ salts. The monolayer of 2(C22)-Ni shows both shapeless and small circular domains. The monolayer of 2(C18)-Ni shows domains that are partially combined with many circular domains. Further, the monolayer of 2(C14)-Ni shows isolated circular domains with a diameter of 200 nm. The monolayers of 2(C12)-Ni salts, which have randomly oriented M(dmit)₂ units, as confirmed by polarized visible spectra, show rather small and unclear domains. However, in the case of monolayer of 2(C10)-Ni, there are no systematic changes in domain size with a change in the chain length, and both large and small domains with diameters in the range of 200 nm to 50 nm are present. That is, it is possible to control the size and shape of mesoscopic domains on the monolayer surface of alkylammonium-M(dmit)₂ salts by changing the chain length, number of hydrophobic chains, and central metal.

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